

Exact results for one dimensional fluids through functional integration

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We review some of the exactly solvable one dimensional continuum fluid models of equilibrium classical statistical mechanics under the unified setting of functional integration in one dimension. We make some further developments and remarks concerning fluids with non pairwise-additive interaction. We then apply our developments to the study of a particular non pairwise-additive Gaussian model for which we are unable to find a well defined thermodynamics.

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I. INTRODUCTION

The physics of one dimensional systems is simpler than that of higher dimensional ones. Specifically the free energy of an interacting gas, a *fluid*, has had an exact solution only in one dimension. The apparent simplicity of restricting motion to one spatial dimension is well known and has had much appeal. But what is the relation between the exactly soluble models of the one dimensional world and the richer and puzzling problems of the three dimensional one? A one dimensional gas was once thought to be incapable even of condensation. Later with the introduction of infinite range forces it has been made to condense, but even so this liquid can never freeze. What one finds is that these models are useful tests of approximate mathematical methods, the solutions of these models are surprisingly complex and interesting, physical applications are often and unexpectedly discovered, and more importantly they educate us to the need of rigorous and exact analysis with which one can have a better definition of reality. The fact that particles can get around each other is responsible for much of the structure of the ordinary world, and is also responsible for the difficulties which the mathematical physicist encounter in studying it. In one dimension we renounce to some of the structure in favor of the possibility of obtaining an exact solution.

The importance of one dimensional physics also lies in the fact that a number of many-body problems in higher dimensions can be accurately mapped into one dimensional problems.

Léon Van Hove showed that one dimensional fluids with impenetrable particles each one interacting with a finite number of neighbors do not have a phase transition at a non zero temperature¹.

In this work I will describe a way of simplifying the calculation of the grand canonical partition function of an ensemble of classical particles living in a one dimensional

world and interacting with a given pair-potential v , originally described by Edwards and Lenard in their paper 2 which I will call EL from now on. Using the notion of a general Gaussian random process and Kac's theorem, they show how it is possible to express the grand partition function as a one dimensional integral of the fundamental solution of a given partial differential equation. The kind of partial differential equation will be fixed by the kind of *diffusion equation* satisfied by the Gaussian random process. In sections II, III, and IV I will present EL's functional integration technique. In subsection V B I will show how, in EL, the properties of the Wiener process are used to solve "Edwards' model" or "Lenard's model". I will then show, in subsection V A, how one can use the properties of the Ornstein-Uhlenbeck process to solve the "Kac-Baker's model".

The main original contribution given in this work lies in section VIII where I show how a generalized Ornstein-Uhlenbeck process can be used to solve models with a more general non pairwise-additive interaction potential. In Section VI I show how EL propose to extract thermodynamical informations from their functional integration treatment and in section VII I show, following EL, how it is possible to reduce the search of the grand partition function, to a characteristic value problem, when the diffusion equation is independent of "time". In section VIII I show how one has to renounce to this reduction, for the generalized Ornstein-Uhlenbeck process satisfying, in general, a non separable diffusion equation. In subsection VIII A I then apply the theoretical framework of such section to a non pairwise-additive penetrable Gaussian interaction model. In particular I will prove that this model is thermodynamically unstable in its attractive version (which is also not H-stable) and I will find an approximate expression for the grand partition function of the repulsive version (which clearly is H-stable) in terms of a triple series one of which is alternating.

More recently³ the functional integral technique of Edwards and Lenard has been used to solve the statistical mechanics of a one dimensional Coulomb gas with boundary interactions as a one dimensional model for a colloidal and soap film.

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I think that the success of the functional integration method described in this work to find exact solutions of the equilibrium classical (non-quantum) statistical mechanics problem of one dimensional fluids has certainly been one of the motivations for the popularity acquired by functional integration after the pioneering developments of Marc Kac and Richard Feynman. The link with the theory of stochastic processes is just a beautiful example of how many different theoretical frameworks come together in the few exact solutions of classical many-body problems.

II. THE PROBLEM

The problem is to simplify the calculation of the grand canonical partition function of a system of particles in the segment $[0, L]$ whose positions are labeled by x_i with $i = 1, 2, \dots, N$, in thermal equilibrium at a reduced temperature θ , namely,

$$\Omega = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int_0^L dx_N \cdots \int_0^L dx_1 e^{-\frac{V_N(x_1, \dots, x_N)}{\theta}}. \quad (2.1)$$

EL consider the total potential energy of the system to be,

$$V_N(x_1, \dots, x_N) = \sum_{i=1}^N \sum_{j=1}^N w(x_i, x_j), \quad (2.2)$$

where $w(x_i, x_j)$ is a function of two variables depending on the pair-potential $v(|x_i - x_j|)$ and the kind of reservoir exchanging particles with the system.

The main idea of EL, is to rewrite the grand partition function as a functional average,

$$\begin{aligned} \Omega &= \left\langle e^{\int_0^L dx' F(\phi(x'))} \right\rangle \\ &= \left\langle \sum_{N=0}^{\infty} \frac{1}{N!} \int_0^L dx_N \cdots \int_0^L dx_1 \prod_{i=1}^N F(\phi(x_i)) \right\rangle. \end{aligned} \quad (2.3)$$

And then choose $F(\phi) = z \exp(i\sigma\phi)$, to get,

$$\Omega = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int_0^L dx_N \cdots \int_0^L dx_1 \left\langle e^{i\sigma \sum_{i=1}^N \phi(x_i)} \right\rangle, \quad (2.4)$$

where in interchanging the average with the sum and the integrals they use the linearity of the average. we haven't defined the average yet so we will do it next.

III. AVERAGING OVER A GENERAL GAUSSIAN RANDOM PROCESS

A general Gaussian random process $\phi(x)$ is defined by the postulate that for any finite number of points x_1, \dots, x_N the joint probability density for $\phi(x_k)$ in $d\phi_k$ (we will often make use of the abbreviation $\phi_i \equiv \phi(x_i)$) is of the form,

$$P(\phi_1, \dots, \phi_N) = \frac{\sqrt{\det B}}{(2\pi)^{N/2}} e^{-\frac{1}{2} \sum_{k=1}^N \sum_{l=1}^N B_{kl} \phi_k \phi_l}, \quad (3.1)$$

where $B_{ij} = B_{ij}(x_1, \dots, x_N)$ are the elements of the positive definite matrix B .

Let α_k be N arbitrary real numbers. Then,

$$\left\langle e^{i \sum_{i=1}^N \alpha_i \phi_i} \right\rangle = e^{-\frac{1}{2} \sum_{k=1}^N \sum_{l=1}^N C_{kl} \alpha_k \alpha_l}, \quad (3.2)$$

where $C = B^{-1}$.

Differentiating with respect to α_k and α_l (not excluding $k = l$) and then setting all α to zero, one obtains,

$$\langle \phi(x_k) \phi(x_l) \rangle = C_{kl} = C(x_k, x_l), \quad (3.3)$$

where C is a function of two variables only, called the *covariance function*. From equations (3.2) and (3.3) follows that also $B_{ij} = B(x_i, x_j)$ is a function of just two variables. The covariance completely characterizes the statistical nature of $\phi(x)$.

Replacing all the α 's in equation (3.2) with σ and comparing (3.2) and (2.4) with (2.1) and (2.2) one recognizes that,

$$C(x_1, x_2) = \frac{2}{\theta \sigma^2} w(x_1, x_2). \quad (3.4)$$

This imposes a restriction to the systems that one can treat. Namely we need w to be positive definite.

Why is all this useful is explained in the next section.

IV. KAC'S THEOREM

Consider a Markoffian process $\phi(x)$, i.e. one for which, given any increasing sequence of “times” x_0, x_1, \dots, x_n , with $x_0 \leq x_1 \leq \dots \leq x_n$, the probability density that $\phi(x_k)$ is in $d\phi_k$ (with $k = 0, 1, \dots, n$) is the product,

$$P(\phi_1, \dots, \phi_n) = \int_{-\infty}^{\infty} \prod_{k=1}^n P(\phi_k, x_k | \phi_{k-1}, x_{k-1}) R(\phi_0, x_0) d\phi_0, \quad (4.1)$$

where $P(\phi_1, x_1 | \phi_0, x_0)$ is the conditional probability that $\phi(x_1)$ is in an element $d\phi_1$ around ϕ_1 given that $\phi(x_0) = \phi_0$ and $R(\phi, x)$ is the initial probability distribution for the process.⁴ Both the conditional probabilities and the initial distribution are assumed to be normalized to unity over the interval $\phi \in [-\infty, +\infty]$,

$$\int_{-\infty}^{\infty} d\phi_1 P(\phi_1, x_1 | \phi_0, x_0) = \int_{-\infty}^{\infty} d\phi R(\phi, x) = 1. \quad (4.2)$$

Any quantity which is an expression involving $\phi(x)$ is a random variable whose average value may be determined using the probability (4.1).

One is interested in averages of the form,

$$\begin{aligned} W(x, x_0) &= \left\langle e^{\int_{x_0}^x dx' F(\phi(x'), x')} \right\rangle \\ &= 1 + \sum_{n=1}^{\infty} \frac{1}{n!} \int_{x_0}^x dx_n \int_{x_0}^x dx_{n-1} \cdots \int_{x_0}^x dx_1 \langle F(\phi_n, x_n) \cdots F(\phi_1, x_1) \rangle \\ &= 1 + \sum_{n=1}^{\infty} \int_{x_0}^x dx_n \int_{x_0}^{x_n} dx_{n-1} \cdots \int_{x_0}^{x_2} dx_1 \langle F(\phi_n, x_n) \cdots F(\phi_1, x_1) \rangle. \end{aligned} \quad (4.3)$$

Kac's theorem takes advantage of the Markoffian property (4.1) to relate to each other the successive terms of this series by an integral-recursion formula. It can be seen by inspection that,

$$\begin{aligned} W(x, x_0) &= \int_{-\infty}^{\infty} d\phi Q(\phi, x | \phi_0, x_0), \\ Q &= \sum_{n=0}^{\infty} Q_n, \\ \begin{cases} Q_0(\phi, x | \phi_0, x_0) = \int_{-\infty}^{\infty} d\phi_0 P(\phi, x | \phi_0, x_0) R(\phi_0, x_0) \\ Q_n(\phi, x | \phi_0, x_0) = \int_{x_0}^x dx' \int_{-\infty}^{\infty} d\phi' P(\phi, x | \phi', x') F(\phi', x') Q_{n-1}(\phi', x' | \phi_0, x_0) \end{cases} \end{aligned} \quad (4.4)$$

Then one can write the following integral equation for Q ,

$$\begin{aligned} Q(\phi, x | \phi_0, x_0) &= Q_0 + \sum_{n=1}^{\infty} Q_n = \int d\phi_0 P R + \sum_{n=1}^{\infty} \int dx' \int d\phi' P F Q_{n-1} \\ &= \int_{-\infty}^{\infty} d\phi_0 P(\phi, x | \phi_0, x_0) R(\phi_0, x_0) + \int_{x_0}^x dx' \int_{-\infty}^{\infty} d\phi' P(\phi, x | \phi', x') F(\phi', x') Q(\phi', x' | \phi_0, x_0). \end{aligned} \quad (4.5)$$

This is the main result of Kac's theorem.

Now assuming that the stochastic process $\phi(x)$ satisfies a forward Fokker-Planck equation,

$$\begin{aligned} \frac{\partial}{\partial x} P(\phi, x | \phi_0, x_0) &= \mathcal{L}(\phi, x) P(\phi, x | \phi_0, x_0) \\ P(\phi, x_0 | \phi_0, x_0) &= \delta(\phi - \phi_0) \quad \text{initial condition} \end{aligned} \quad (4.6)$$

that Q satisfies,

$$\begin{aligned} \frac{\partial}{\partial x} Q(\phi, x | \phi_0, x_0) &= [\mathcal{L}(\phi, x) + F(\phi, x)] \times \\ &\quad Q(\phi, x | \phi_0, x_0) \\ Q(\phi, x_0 | \phi_0, x_0) &= R(\phi, x_0) \quad \text{initial condition} \end{aligned} \quad (4.7)$$

it immediately follows from the integral formula (4.5),

If we now further assume $\phi(x)$ to be a Gaussian process (so that equation (4.1) is of the form (3.1)) then we can

put together the result of the previous section (3.4) and Kac's theorem, to say that,

$$\Omega = W(L, 0) = \int_{-\infty}^{\infty} d\phi Q(\phi, L|0, 0), \quad (4.8)$$

where $Q = Q(\phi, x|\phi_0, x_0)$ is the solution of the partial differential equation (4.7) with $F(\phi, x) = F(\phi) = z \exp(i\sigma\phi)$. This is the simplification found by EL.

Note the following points:

- This certainly is a simplification from a computational point of view and establishes a bridge between non-equilibrium statistical mechanics and the theory of stochastic processes and equilibrium statistical mechanics in one dimension.
- When the operator \mathcal{L} is independent of “time” (we keep calling x time because it comes natural from the notion of random process. In the present context though x is the position of a particle along his one dimensional world) then both $P(\phi, x|\phi_0, x_0)$ and $Q(\phi, x|\phi_0, x_0)$ depend only on $|x - x_0|$ since F does not depend explicitly on x .
- For a non-stationary random process $\phi(x)$ it is often possible to choose a delta function as initial distribution, i.e. $R(\phi, x_0) = \delta(\phi - \phi_0)$, where $\phi_0 = \phi(x_0)$. In this case Q is the *fundamental solution* of the partial differential equation (4.7).
- For a non-stationary random process the covariance function $C(x_1, x_2) = \langle \phi(x_1)\phi(x_2) \rangle$ is not a function of $|x_2 - x_1|$ alone. The identification of the covariance with the pair-potential v demands that the process be stationary because the pair-potential is a function of the difference of the two position variables. But in some cases (due for example to the presence of the reservoir) w may differ from v (see subsection V B).

As a final remark, in EL is stressed the importance of the Markoffian nature of the process. They observe that the concept of a Markoffian process involves the idea of a succession in “time” and this is meaningless when there is more than one independent variable. So it seems to be hard to extend the technique just described even to a two dimensional system.

In the following section we will apply the functional integration technique just described to some concrete example.

V. EXAMPLES

Note that due to the Markoffian nature of the stochastic process the following two properties should be re-

quired for $x_0 \leq x_1 \leq x_2$,

$$R(\phi_1, x_1) = \int_{-\infty}^{\infty} d\phi_0 P(\phi_1, x_1|\phi_0, x_0) R(\phi_0, x_0), \quad (5.1)$$

$$P(\phi_2, x_2|\phi_0, x_0) = \int_{-\infty}^{\infty} d\phi_1 P(\phi_2, x_2|\phi_1, x_1) P(\phi_1, x_1|\phi_0, x_0). \quad (5.2)$$

Let us see now how all this works for two well known Markoffian, Gaussian stochastic processes.

A. The Ornstein-Uhlenbeck process

The *Ornstein-Uhlenbeck process* is a stationary process defined as follows,

$$R(\phi_0, x_0) = \frac{e^{-\frac{\phi_0^2}{2}}}{\sqrt{2\pi}}, \quad (5.3)$$

$$P(\phi, x|\phi_0, x_0) = \frac{e^{-\frac{(\phi - \phi_0 e^{-\gamma\Delta x})^2}{2S(\Delta x)}}}{\sqrt{2\pi S(\Delta x)}}, \quad (5.4)$$

$$\text{with } \Delta x = |x - x_0|, \\ S(\Delta x) = 1 - e^{-2\gamma\Delta x},$$

where γ is the inverse of the characteristic time constant of the process, i.e. a positive real number.

The covariance for this process is,

$$C(x_1, x_2) = e^{-\gamma|x_1 - x_2|}. \quad (5.5)$$

The Fokker-Planck equation satisfied by the process is the Smoluchowski diffusion equation for an harmonic oscillator,

$$\mathcal{L}(\phi) = \gamma \left(\frac{\partial^2}{\partial \phi^2} + \frac{\partial}{\partial \phi} \phi \right). \quad (5.6)$$

So this process can be used to describe a system of particles whose potential energy is,

$$w(x_1, x_2) = \frac{\theta\sigma^2}{2} e^{-\gamma|x_1 - x_2|}. \quad (5.7)$$

Adding a hard-core part to this long range potential and making it attractive by choosing σ pure imaginary, gives the so called “Kac-Baker model”. Yang and Lee showed that the presence of the hard core part is sufficient to ensure the existence of the thermodynamic potential for the infinite system ($L \rightarrow \infty$). This was calculated exactly by Kac who also proved that the model has no phase transitions (because of the infinite range of the potential, L. Van Hove's proof is not applicable here). Later Baker showed that if one sets,

$$\sigma = i\sqrt{\frac{\alpha_0\gamma}{\theta}}, \quad (5.8)$$

(so that the integral of the potential is independent of γ) and then takes the limit $\gamma \rightarrow 0$ after the limit $L \rightarrow \infty$,

then a phase transition of the classical Van der Waals type is obtained. A model with exponential repulsive pair-potential (exactly like the one in (5.7)) was studied by D. S. Newman, who concluded that it did not show phase transitions in the long range limit $\gamma \rightarrow 0$.⁵

B. The Wiener process

We follow EL and introduce the *Wiener process*. It is a non-stationary process defined by (if $x \geq x_0 > 0$),

$$R(\phi_0, x_0) = \frac{e^{-\frac{\phi_0^2}{4Dx_0}}}{\sqrt{4\pi Dx_0}} \quad (5.9)$$

$$P(\phi, x | \phi_0, x_0) = \frac{e^{-\frac{\Delta\phi^2}{4D\Delta x}}}{\sqrt{4\pi D\Delta x}}, \quad (5.10)$$

$$\begin{aligned} \text{with } \Delta x &= x - x_0, \\ \Delta\phi &= \phi - \phi_0, \end{aligned}$$

where D is the diffusion constant of the Brownian process, i.e. a positive real number.

The covariance for this process is,

$$C(x_1, x_2) = 2D \min(x_1, x_2). \quad (5.11)$$

Although this process cannot be differentiated it can be seen as the integral, $\phi(x) = \int_0^x ds \xi(s)$, of the Gaussian white noise process, $\xi(x)$, defined by $\langle \xi(x) \rangle = 0$ and $\langle \xi(x_1)\xi(x_0) \rangle = \zeta^2 \delta(x_1 - x_0)$ and the attribute Gaussian implies that all cumulants higher than of second order vanish. One just needs to set $2D = \zeta^2$.

The Fokker-Planck equation satisfied by the process is the Einstein diffusion equation,

$$\mathcal{L}(\phi) = D \frac{\partial^2}{\partial \phi^2}. \quad (5.12)$$

So this process can be used to describe a system of particles whose potential energy is,

$$w(x_1, x_2) = D\theta\sigma^2 \min(x_1, x_2). \quad (5.13)$$

It was S. F. Edwards, see EL, who first realized that this is a Coulomb system: electrons of charge q living in the segment $[0, L]$ are in contact with an infinite reservoir (in the region $x < 0$, say). The reservoir exchanges particles with the system of electrons giving rise to the statistical fluctuations in particle number. Take the system plus reservoir electrically neutral as a whole and imagine the system containing N electrons. Then there is a total charge $-Nq$ in the reservoir. Gauss theorem then tells that in the region $x \geq 0$ there is a constant electric field of magnitude $2\pi Nq$, due to the presence of the reservoir. Now choosing,

$$D = \frac{2\pi}{\theta}, \quad (5.14)$$

$$\sigma = q, \quad (5.15)$$

one can rewrite the total potential energy of the system as,

$$\begin{aligned} V_N &= 2\pi q^2 \sum_{k=1}^N \sum_{l=1}^N \min(x_k, x_l) \\ &= 2\pi q^2 \sum_{k=1}^N \sum_{l=1}^N \left[-\frac{|x_k - x_l|}{2} + \frac{x_k + x_l}{2} \right] \\ &= -2\pi q^2 \sum_{k < l} |x_k - x_l| + 2\pi q^2 \sum_{k=1}^N \sum_{l=1}^N x_l \\ &= -2\pi q^2 \sum_{k < l} |x_k - x_l| + 2\pi Nq^2 \sum_{l=1}^N x_l. \end{aligned} \quad (5.16)$$

Which is readily recognized as the expected result for the ‘‘Edwards’ model’’. We are assuming that the line is the real world in which each charge lives. So that also its field lines cannot escape from the line. Then the electric potential of each charge is the solution of $d^2\psi(x)/dx^2 = -4\pi\delta(x)$, i.e. $\psi(x) = -2\pi|x|$.

Note that due to the presence of the neutralizing reservoir, w is not just a function of $|x_i - x_j|$ and consequently the random process is not just a stationary one as in the Kac-Baker example.

In this case Edwards has not been able to answer in a definite way to the problem of continuity of the thermodynamic functions.

VI. THERMODYNAMICS

Following EL, we want now comment briefly on the relevance of all this from the point of view of the thermodynamics of the system of particles. Given the grand canonical partition function $\Omega = \Omega(z, L, \theta)$ the equation of state follows from eliminating z between the two following equations,

$$\frac{P}{\theta} = \frac{1}{L} \ln \Omega(z, L, \theta), \quad (6.1)$$

$$n = z \frac{\partial}{\partial z} \frac{1}{L} \ln \Omega(z, L, \theta). \quad (6.2)$$

where P is the pressure and n the number density of particles. Sometimes one talks about *chemical potential* μ (of the one-component system), instead of z . The two are related by,

$$z = \left(\frac{m\theta}{2\pi\hbar^2} \right)^{1/2} e^{\mu/\theta} > 0, \quad (6.3)$$

where m is the mass of the particles. All the other thermodynamic functions can be obtained from the internal energy,

$$U(N, L, S) = -\frac{\partial}{\partial(1/\theta)} \ln \Omega(z, L, \theta) + \frac{1}{2}N\theta, \quad (6.4)$$

where S is the entropy of the system. Or alternatively from the Helmholtz free energy,

$$A(N, L, \theta) = \mu N - \theta \ln \Omega(z, L, \theta). \quad (6.5)$$

It is often useful to simplify the problem by studying just the asymptotic behavior of Ω in the infinite system limit $L \rightarrow \infty$. This usually allows the recognition of eventual phase transitions (as in the Yang and Lee theory and L. Van Hove theorem) as singularities in the equation of state. The equation of state for the infinite system becomes then,

$$\left\{ \begin{array}{l} \frac{P}{\theta} = \Phi(z, v, \theta) = \lim_{L \rightarrow \infty} \left[\frac{1}{L} \ln \Omega(z, L, \theta) \right], \\ n = \frac{1}{v} = \lim_{L \rightarrow \infty} \left[z \frac{\partial}{\partial z} \frac{1}{L} \ln \Omega(z, L, \theta) \right], \end{array} \right. \quad (6.6)$$

where the limit may not be freely interchanged with the differentiation.

VII. CHARACTERISTIC VALUE PROBLEM

Both the examples described have the common feature that \mathcal{L} is independent of time x . Under this circumstance the problem of calculating the grand canonical partition function Ω may be simplified even further, as shown in EL.

Letting $\phi \rightarrow \phi/\sigma$, the coefficient function $F(\phi)$ in equation (4.7) is periodic with period 2π . It is then possible to reduce the problem (4.7) to the characteristic value problem of an ordinary differential operator on a finite interval of the independent variable ϕ . Let,

$$\tilde{Q}(\phi, x) = \sum_{n=-\infty}^{\infty} Q(\phi + 2\pi n, x|0, 0). \quad (7.1)$$

This function is the *periodic solution* of the partial differential equation (4.7) and for $x = 0$ it reduces to,

$$\tilde{Q}(\phi, 0) = \sum_{n=-\infty}^{\infty} R(\phi + 2\pi n, 0). \quad (7.2)$$

For the “Kac-Baker model” one finds for example $\tilde{Q}(\phi, 0) = \theta_3(i\pi\phi/\sigma^2, e^{-2\pi^2/\sigma^2}) e^{-\phi^2/2\sigma^2}/\sqrt{2\pi\sigma^2}$, where θ_3 is an elliptical theta function⁶, and for the “Edwards’ model” $\tilde{Q}(\phi, 0) = \sum_{n=-\infty}^{\infty} \delta(\phi + 2\pi n)$. So, for this latter case, \tilde{Q} is the *periodic fundamental solution* of (4.7). It then follows that,

$$\Omega = \int_{-\pi}^{\pi} d\phi \tilde{Q}(\phi, L). \quad (7.3)$$

Since F and \mathcal{L} do not depend on x , in solving (4.7) for \tilde{Q} , one may use the method of separation of variables. This leads to the characteristic value problem,

$$\begin{aligned} [\mathcal{L}(\phi) + F(\phi)] y(\phi) &= \lambda y(\phi), \\ y(\phi + 2\pi) &= y(\phi). \end{aligned} \quad (7.4)$$

Then one looks for a complete orthonormal set of eigenfunctions y_m with relative eigenvalues λ_m ($m = 0, 1, 2, \dots$),

$$\int_{-\pi}^{\pi} d\phi y_m(\phi) y_{m'}(\phi) = \delta_{m,m'}. \quad (7.5)$$

The expansion of \tilde{Q} in terms of these functions is,

$$\tilde{Q}(\phi, x) = \sum_{m=0}^{\infty} e^{\lambda_m x} B_m y_m(\phi), \quad (7.6)$$

$$B_m = \int_{-\pi}^{\pi} d\phi \tilde{Q}(\phi, 0) y_m(\phi). \quad (7.7)$$

For example $B_m = y_m(0)$ for the “Edwards’ model”. The grand partition function becomes,

$$\Omega(L) = \sum_{m=0}^{\infty} A_m e^{\lambda_m L}, \quad (7.8)$$

$$A_m = B_m \int_{-\pi}^{\pi} d\phi y_m(\phi). \quad (7.9)$$

The λ_m and the y_m depends parametrically on z which enters into the definition of $F(\phi)$. Moreover since $F(\phi) = F^*(-\phi)$ the λ_m are either real or occur in complex conjugate pairs.

Now assume that among the sequence of eigenvalue λ_m there is one λ_0 that is real and is bigger than the real part of all the others then the following simplification holds,

$$\boxed{\Omega(L \rightarrow \infty) \sim A_0 e^{\lambda_0 L}}. \quad (7.10)$$

The equation of state for the infinite system then becomes,

$$P = \theta \lambda_0(z), \quad (7.11)$$

$$\begin{aligned} n &= \lim_{L \rightarrow \infty} \left[z \frac{\partial}{\partial z} \left(\frac{\ln A_0(z)}{L} + \lambda_0(z) \right) \right] \\ &= z \frac{\partial}{\partial z} \lambda_0(z). \end{aligned} \quad (7.12)$$

For example for the ideal gas, $\sigma \rightarrow 0$ and $\lambda_0(z) = az$, with a a constant.

Let us summarize the characteristic value problem for the examples described. Denoting with a dash a first derivative respect to ϕ ($\dots' \equiv d\dots/d\phi$) we have:

(i) “Kac-Baker model” repulsive⁵,

$$\gamma[\sigma^2 y'' + (\phi y)'] + z e^{i\phi} y = \lambda y, \quad (7.13)$$

(ii) “Edwards’ model”²,

$$\frac{2\pi q^2}{\theta} y'' + z e^{i\phi} y = \lambda y, \quad (7.14)$$

this is the one component plasma or *jellium* system.

(iii) “Lenard’s model”⁷,

$$\frac{2\pi q^2}{\theta} y'' + 2z \cos(\phi) y = \lambda y, \quad (7.15)$$

this is the two component plasma system of two kinds of particles with charges $\pm q$ and the corresponding values of z that by symmetry may be assumed equal without loss of generality.

In all cases $y(\phi)$ is a function of period 2π (for the attractive Kac-Baker model the periodicity is lost but the characteristic value problem is still valid).

Unfortunately there is no simple way to solve explicitly Eq. (7.13) for the Kac-Baker model. Nonetheless it is apparent the existence of the thermodynamic limit for the repulsive model, as was proved by D. S. Newman⁸.

In the Edwards' model the presence of the neutralizing reservoir is responsible (the potential energy of interaction between the particles and the reservoir being proportional to $+x$) for the charges all of the same sign to accumulate at the origin resulting in a system with zero density and pressure in accord with the fact that Eq. (7.14) admits solutions in terms of modified Bessel functions of the first kind $I_{\pm i\sqrt{2\theta\lambda/\pi q^2}}(\sqrt{2\theta z e^{i\phi}/\pi q^2})$ which form a complete set for $\lambda = -m^2$ with $m = 0, 1, 2, \dots$, so that $\lambda_0 = 0$.

In the Lenard's model the solutions of Eq. (7.15) is in terms of even and odd Mathieu functions with characteristic value $a = -2\lambda\theta/\pi q^2$, parameter $q = -2\theta z/\pi q^2$, and argument $\phi/2$. According to Floquet's theorem, any Mathieu function of argument ϕ can be written in the form $e^{ir\phi}f(\phi)$, where f has period 2π and r is the *Mathieu characteristic exponent*. For nonzero q the Mathieu functions are only periodic for certain values of a . Such *Mathieu characteristic values* are given by $a_r = A(r, q)$ with r integer or rational and $A(0, q) \leq A(r, q)$ for all r, q . Then we will have $\lambda_0 = -(\pi q^2/2\theta)A(0, -2\theta z/\pi q^2)$. In Fig. 1 we show the equation of state of the Lenard model at various temperatures θ for $q = 1$. We are then

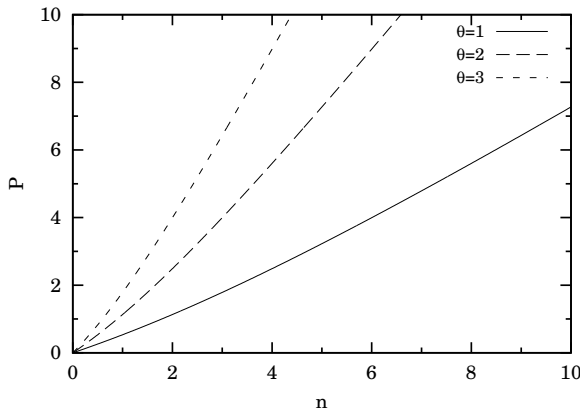


FIG. 1. The equation of state for the Lenard's model at various temperatures θ for $q = 1$.

led to conclude that this system does not admit any phase transition, condensation (gas-liquid) or freezing (liquid-solid).

VIII. A NON PAIRWISE-ADDITIVE PENETRABLE INTERACTION MODEL

In the examples described we started from known stochastic processes to find which physical fluid model they may be able to describe. Actually one wants to do the reverse: given a physical model, i.e. given w (a positive definite function (3.4)), determine the stochastic process that allows the desired simplification for the grand canonical partition function.

In the more general case one has to deal with w 's which are not functions of the pair-potential alone, as happened in the case of Edwards' model. For example one may be interested in modifying Edwards' model for the case of a Coulomb system moving but not living in $[0, L]$ with field lines allowed to exit the segment and interacting with the full three dimensional pair-potential $v(x) = 1/\sqrt{x^2 + \varepsilon^2}$, with ε a small positive quantity so that $v_0 = 1/\varepsilon$ or $\sigma = 2/\sqrt{\varepsilon\theta}$. A neutralizing uniform background in this case gives rise to quadratic terms making even the one-component system stable. To obtain the purely one dimensional case it is necessary to take the $\varepsilon \rightarrow 0$ limit at the end of the analysis of the *quasi one dimensional* case. This problem has been solved by R. J. Baxter⁵ who developed a method for finding the partition function when the pair-potential satisfies a linear differential equation with constant coefficients. His method still leads to an eigenvalue problem but does not employ functional averaging.

As a progress in this direction it is useful to reconsider the Ornstein-Uhlenbeck process in a more general way. Consider the following stationary stochastic process,

$$R(\phi_0, x_0) = \frac{e^{-\frac{\phi_0^2}{2}}}{\sqrt{2\pi}}, \quad (8.1)$$

$$P(\phi, x|\phi_0, x_0) = \frac{e^{-\frac{(\phi - \phi_0 A(\Delta x))^2}{2S(\Delta x)}}}{\sqrt{2\pi S(\Delta x)}}, \quad (8.2)$$

$$\text{with } \Delta x = |x - x_0|, \\ S(\Delta x) = 1 - A^2(\Delta x),$$

where the last definition assures the validity of the Markoffian property (5.1). Clearly, in order to satisfy the Markoffian property (5.2) we need to require $A(x)A(y) = A(x+y)$ which is only satisfied by choosing A as an exponential as in the Ornstein-Uhlenbeck process. Here we willingly violate this second property and choose A as an arbitrary function. In order to have $P(\phi, x_0|\phi_0, x_0) = \delta(\phi - \phi_0)$ we must also require that $\lim_{x \rightarrow 0} A(x) = 1$.

The covariance for this process is,

$$C(x_i, x_j) = \frac{2}{\theta\sigma^2} w(x_i, x_j) = \prod_{k=i}^{j-1} A(|x_k - x_{k+1}|), \quad (8.3)$$

with $x_i \leq x_{i+1} \leq x_{i+2} \leq \dots \leq x_j$. So the interaction between particle i and particle j depends on how

many particles lie between them. This is a particular *non pairwise-additive* interaction model.

It can be readily verified that the transition density of this process satisfies the following forward Fokker-Planck equation,

$$\mathcal{L}(\phi, x) = -\frac{\dot{A}}{A} \left(\frac{\partial^2}{\partial \phi^2} + \frac{\partial}{\partial \phi} \right), \quad (8.4)$$

where the dot denotes differentiation with respect to time ($\dot{} \equiv d/dx$). All the properties of section IV continue to hold. Then, calling $v = A\theta\sigma^2/4$ with $v(0) = v_0 = \theta\sigma^2/4$, i.e. *penetrable* particles, we can simplify the thermodynamics of a fluid with the following potential energy

$$V_N = \sum_{i < j} \prod_{k=i}^{j-1} v(|x_k - x_{k+1}|), \quad (8.5)$$

for a configuration with $x_1 \leq x_2 \leq x_3 \leq \dots \leq x_N$.

Unfortunately in this case we cannot use the method of separation of variables described in section VII since \mathcal{L} is time dependent.

Introducing the function $B^2(x) = -2d \ln A(x)/dx$ one can then say that according to Ito or Stratonovich calculus⁹ the process defined by Eqs. (8.1)-(8.2) satisfies the following stochastic differential equation,

$$\dot{\phi}(x) = -\frac{B^2(x)}{2}\phi(x) + B(x)\xi(x), \quad (8.6)$$

where $\xi(x)$ is Gaussian white noise with $\zeta = 1$. The $\xi(x)$ can be generated on a computer as pseudo random numbers on a large interval $\xi \in [-a, a]$ with a big enough.

A. Example: A non pairwise-additive Gaussian model

For example we want to simplify the non pairwise-additive interaction model fluid of the previous section,

Eq. (8.5), with $v(x) = v_0 e^{-\gamma x^2}$, $\gamma > 0$, a *Gaussian core model*. In this case we have $A(x) = e^{-\gamma x^2}$ and $B^2(x) = 4\gamma x$. For this model we expect that the attractive, $\sigma^2 = 4v_0/\theta < 0$, case is thermodynamically unstable in agreement with the fact that the particles will tend to collapse at a same point since the system is not H-stable in the sense of Ruelle¹⁰. On the other hand we do not know anything yet about the repulsive, $\sigma^2 > 0$, case, which is H-stable and therefore we must have $P/\theta < z$. For example, we know that there cannot be any condensation but an interesting question is whether there can be freezing¹¹.

The problem (4.7) becomes

$$\frac{\partial}{\partial x} \tilde{Q}(\phi, x) = \left[2\gamma x \left(\sigma^2 \frac{\partial^2}{\partial \phi^2} + \frac{\partial}{\partial \phi} \right) + z e^{i\phi} \right] \times \tilde{Q}(\phi, x), \quad (8.7)$$

$$\tilde{Q}(\phi, 0) = \theta_3 \left(i\pi\phi/\sigma^2, e^{-2\pi^2/\sigma^2} \right) \frac{e^{-\frac{\phi^2}{2\sigma^2}}}{\sqrt{2\pi\sigma^2}}, \quad (8.8)$$

with $\tilde{Q}(\phi + 2\pi, x) = \tilde{Q}(\phi, x)$. This is a non-separable partial differential equation. Again the grand canonical partition function is given by Eq. (7.3),

$$\Omega = \int_{-\pi}^{\pi} d\phi \tilde{Q}(\phi, L).$$

Clearly, approximating $F(\phi) \approx z$ or, equivalently, setting $\sigma \rightarrow 0$, we get the ideal gas behavior. In fact the solution to Eq. (8.7) is, in this simple case, $Q(\phi, x|0, 0) = P(\phi, x|0, 0)e^{zx}$, since $\partial P/\partial x = \mathcal{L}P$. So that from Eqs. (4.8) and (4.2) immediately follows $\Omega = e^{zL}$.

In order to make some progress towards the solution of the full Eq. (8.7) we define $\mathcal{L} \equiv x\mathcal{R}$ and $\mathcal{H}(x) = x\mathcal{R} + F$. Since \mathcal{H} at different times do not commute we use the following Dyson series

$$Q(\phi, x|0, 0) = \mathcal{U}(x, 0)R(\phi, 0), \quad (8.9)$$

$$\mathcal{U}(x, x_0) = 1 + \sum_{n=1}^{\infty} \int_{x_0}^x dx_n \int_{x_0}^{x_n} dx_{n-1} \cdots \int_{x_0}^{x_2} dx_1 \mathcal{H}(x_n) \cdots \mathcal{H}(x_1),$$

Where R is given by Eq. (8.1). So that we find $\Omega = 1 + \sum_{n=1}^{\infty} c_n$ with

$$c_n = \int_0^L dx_n \int_0^{x_n} dx_{n-1} \cdots \int_0^{x_2} dx_1 \int_{-\infty}^{\infty} d\phi \mathcal{H}(x_n) \cdots \mathcal{H}(x_1) R(\phi, 0). \quad (8.10)$$

Solving for c_n we easily find $c_n = \sum_{k=1}^n a_{n,k}$ with

$$a_{n,k} = \frac{e^{-k^2\sigma^2/2} f_{n,k}(\sigma^2) \gamma^{n-k} L^{2n-k} z^k}{k!}, \quad (8.11)$$

with $f_{n,n} = 1$, $f_{n,1} = 0$ for $n > 1$ and $f_{n,k}(\psi)$ a polynomial of degree $n - k$ in ψ beginning with the monomial of

degree one and the others of alternating signs. So

$$\begin{aligned}
\Omega &= 1 + \sum_{n=1}^{\infty} \sum_{k=1}^n a_{n,k} = 1 + \sum_{k=1}^{\infty} \sum_{n=k}^{\infty} a_{n,k} \\
&= 1 + \sum_{k=1}^{\infty} \frac{e^{-k^2 \sigma^2 / 2} (zL)^k}{k!} \sum_{n=k}^{\infty} f_{n,k}(\sigma^2) (\gamma L^2)^{n-k} \\
&= 1 + \sum_{k=1}^{\infty} \frac{(zL)^k}{k!} h_k(\sigma^2, \gamma L^2) = \Omega(zL, \sigma^2, \gamma L^2),
\end{aligned} \tag{8.12}$$

where we defined

$$h_k(\psi, \eta) \equiv e^{-k^2 \psi / 2} g_k(\psi, \eta), \tag{8.13}$$

$$g_k(\psi, \eta) \equiv \sum_{m=0}^{\infty} f_{k+m,k}(\psi) \eta^m. \tag{8.14}$$

First of all notice that, if the thermodynamic limit exists, we must have $P = O(z^2/\gamma, \sigma^2)z\theta$ with O a given function of two variables such that $\lim_{\sigma \rightarrow 0} O(a, \sigma^2) = 1$. Note that when there is no interaction between the particles $v_0 \rightarrow 0$ and/or at very high temperature $\theta \rightarrow \infty$, then $\sigma \rightarrow 0$ and we end up with an ideal gas.

Then, if it was $h_k = 1$ we would immediately find the ideal gas behavior. On the other hand if it was $g_k = 1$ we would find an unstable system for $v_0 < 0$ and a stable system with $P = 0 = n$ for $v_0 > 0$ since

$$\frac{1}{L} \ln \left[\sum_{k=0}^{\infty} \frac{e^{-k^2 \sigma^2 / 2} (zL)^k}{k!} \right] \rightarrow \begin{cases} 0 & \sigma^2 > 0 \text{ for } L \rightarrow \infty \\ \infty & \sigma^2 < 0 \text{ for any } L \end{cases}. \tag{8.15}$$

We then need to find the true h_k or g_k . We already know that $g_1 = 1$. What can we say about $g_k(\psi, \eta)$ for $k > 1$? By inspection of the first few terms of the Dyson series we find that $g_k(\psi, \eta) = 1 + \sum_{m=1}^{\infty} f_{k+m,k}(\psi) \eta^m$ with $f_{k+m,k}(\psi) = \sum_{i=1}^m (-1)^{m+i} d_{k+m,k,i} \psi^i$ and $d_{k+m,k,i}$ some positive coefficients. So that of course $h_k(0, \eta) = 1$ for all k , as it should. Now we can write

$$\begin{aligned}
g_k(\psi, \eta) &= 1 + \sum_{m=1}^{\infty} \sum_{i=1}^m d_{k+m,k,i} (-\psi)^i (-\eta)^m = 1 + \sum_{i=1}^{\infty} (-\psi)^i \sum_{m=i}^{\infty} d_{k+m,k,i} (-\eta)^m \\
&= 1 + \sum_{i=1}^{\infty} l_{k,i}(\eta) (-\psi)^i,
\end{aligned} \tag{8.16}$$

where we defined

$$l_{k,i}(\eta) \equiv \sum_{m=i}^{\infty} d_{k+m,k,i} (-\eta)^m. \tag{8.17}$$

We start looking for the coefficients for $i = 1$. By inspection of the first seven n we find, for $2 \leq k \leq n-1$,

$$d_{n,k,1} = 2^n \frac{k!}{n!} b_{n,k}, \tag{8.18}$$

$$\frac{b_{n,k}}{b_{n,k+1}} = (k-1) R_{n-k+2}, \tag{8.19}$$

$$b_{n,n-1} = \binom{n}{n-3} \frac{1}{2^n}. \tag{8.20}$$

So that

$$b_{n,k} = b_{n,n-1} \frac{(n-3)!}{(k-2)!} \prod_{q=k}^{n-2} R_{n-q+2}, \tag{8.21}$$

and

$$d_{n,k,1} = \frac{k(k-1)}{3!} r_{n-k}, \tag{8.22}$$

with, for $2 \leq k \leq n-2$,

$$r_{n-k} = \prod_{p=4}^{n-k+2} R_p, \tag{8.23}$$

$$r_2 = 4/(2 \cdot 2 + 1)!!,$$

$$r_3 = 8 \cdot 3/4(2 \cdot 3 + 1)!!,$$

$$r_4 = 16 \cdot 3/5(2 \cdot 4 + 1)!!,$$

$$r_5 = 32 \cdot 3/6(2 \cdot 5 + 1)!!,$$

and so on. We can then guess that

$$r_m = \frac{2^m 3}{(2m+1)!!(m+1)}. \tag{8.24}$$

Then we can easily re-sum the series of Eq. (8.17) to say

that

$$l_{k,1}(\eta) = k(k-1) \times \frac{{}_2F_2(\{1,1\}, \{3/2, 2\}, -x) - 1}{2}, \quad (8.25)$$

with ${}_2F_2$ a hyper-geometric function. We also find $\lim_{\eta \rightarrow \infty} l_{k,1}(\eta) = -k(k-1)/2$. What about $l_{k,i}(\eta)$ for $i > 1$?

Their determination is quite laborious but let us suppose first that we had found for $l_{k,i}$,

$$l_{k,i}(\eta) = \frac{1}{i!} \left(\frac{k^2}{2} \right)^i \left(\frac{-\eta}{1+\eta} \right)^i. \quad (8.26)$$

Then it would follow

$$h_k(\psi, \eta) = e^{-\frac{k^2}{2}\psi} e^{\frac{k^2}{2}\frac{\psi\eta}{1+\eta}} = e^{-\frac{k^2}{2}\frac{\psi}{1+\eta}}, \quad (8.27)$$

and for the partition function we would find

$$\Omega_L(z) = \sum_{k=0}^{\infty} \frac{(zL)^k}{k!} e^{-\frac{k^2}{2}\frac{\sigma^2}{1+\gamma L^2}}. \quad (8.28)$$

We could then immediately say that the attractive, $\sigma^2 < 0$, case would be thermodynamically unstable since the series in Eq. (8.28) would be not summable, whereas the repulsive, $\sigma^2 > 0$, case would be stable. In this latter case $O = \lim_{L \rightarrow \infty} \ln \Omega_L/L$ would be finite and the system would admit a well defined thermodynamic limit without phase transitions. The equation of state would be

$$\frac{P}{\theta} = \lim_{L \rightarrow \infty} \frac{\ln \Omega_L(z)}{L} = O(z/\sqrt{\gamma}, \sigma^2) \sqrt{\gamma}, \quad (8.29)$$

$$n = \lim_{L \rightarrow \infty} z \frac{\Omega_L \left(z e^{-\frac{\sigma^2}{1+\gamma L^2}} \right)}{\Omega_L(z)} e^{-\frac{\sigma^2}{2(1+\gamma L^2)}} = z, \quad (8.30)$$

so that $P = O(n^2/\gamma, v_0/\theta)n\theta$ and for small n one would have $P \approx n\theta$.

In order to make some progress towards the exact solution we can then write $d_{n,k,i} = d_{n,k,1}E_{n,k,i}$ and note that $E_{n,k,1} = 1$ and by inspection $E_{2+i,2,i} = 1$. Now if we had $E_{n,k,i} = 1$ for all n, k, i then we would get

$$l_{k,i}(\eta) = \frac{k(k-1)2^{i-1}(-\eta)^i}{(i+1)(2i+1)!!} \times {}_2F_2(\{1, 1+i\}, \{3/2+i, 2+i\}, -\eta). \quad (8.31)$$

We can then use the following limit

$$\lim_{\eta \rightarrow \infty} \frac{{}_2F_2(\{1, 1+i\}, \{3/2+i, 2+i\}, -\eta)\eta}{(i+1)(2i+1)} = \frac{2i}{2i}, \quad (8.32)$$

to say that

$$\lim_{\eta \rightarrow \infty} \frac{l_{k,i}(\eta)}{(-\eta)^{i-1}} = -\frac{k(k-1)2^{i-2}}{i(2i-1)!!}. \quad (8.33)$$

Since, according to Eqs. (8.33) and (8.16), in the large η limit,

$$g_k(\psi, \eta) \rightarrow 1 + k(k-1)\psi \times {}_2F_2(\{1, 1\}, \{3/2, 2\}, \psi\eta)/2, \quad (8.34)$$

for the repulsive, $\sigma^2 > 0$, system we would find

$$\frac{P}{\theta} = \lim_{L \rightarrow \infty} \frac{\ln [{}_2F_2(\{1, 1\}, \{3/2, 2\}, \sigma^2\gamma L^2)]}{L} = \begin{cases} \infty & \sigma^2\gamma & \text{independent of } L \\ \alpha & \sigma^2\gamma L = \alpha & \text{independent of } L \\ 0 & \sigma^2\gamma L^2 & \text{independent of } L \end{cases} \quad (8.35)$$

and $n = 0$. So that in the first two cases we would violate the H-stability condition according to which $P/\theta < z$. This is a signal that our approximation is too brute.

In the appendix we report the first few exact $E_{n,k,i}$. Even if we found it too hard to guess the full analytic expression from the first few of them, the results of the appendix can be used to refine our analysis.

Our final expression for the partition function is

$$\Omega = \sum_{k=0}^{\infty} \frac{e^{-\sigma^2 k^2/2} (zL)^k}{k!} \left(1 + k(k-1) \sum_{i=1}^{\infty} (\sigma^2\gamma L^2)^i \times \sum_{l=0}^{\infty} (-\gamma L^2)^l \frac{E_{k+l+i,k,i} 2^{l+i}}{2(l+i+1)(2(l+i)+1)!!} \right) \quad (8.36)$$

$$\begin{cases} < e^{zL} & \sigma^2 > 0, \\ = \infty & \sigma^2 < 0, \end{cases} \quad (8.37)$$

Note that the dependence of $E_{k+m,k,i}$ on k is crucial because otherwise we could immediately conclude that the pressure would be independent from z . And this fact, added to the H-stability condition $P/\theta < z$, would be enough to say that the repulsive Gaussian core model only admits a zero pressure zero density state. Note also that the dependence of $E_{n,k,i}$ on i is also crucial because otherwise for $\sigma = 1$ the argument of the first two series would be symmetric under exchange of i and l which would mean that the two models with $\gamma > 0$ and with $\gamma < 0$ would have the same thermodynamics which is clearly absurd¹².

The first alternating series has very slow numerical convergence as L grows. We then found it difficult to extract even a numerical equation of state. Nonetheless we found that the triple series is convergent at least in the high temperature regime, $0 < \sigma^2 \ll 1$.

From the H-stability condition (8.37) we find that for any L and $k > 1$ we must have

$$\begin{aligned} & \frac{-1}{k(k-1)} \\ & \leq \sum_{i=1}^{\infty} (\sigma^2\gamma L^2)^i \sum_{l=0}^{\infty} (-\gamma L^2)^l \frac{E_{k+l+i,k,i} 2^{l+i}}{2(l+i+1)(2(l+i)+1)!!} \\ & = \sum_{m=1}^{\infty} (-\gamma L^2)^m \frac{2^m \sum_{i=1}^m (-\sigma^2)^i E_{k+m,k,i}}{2(m+1)(2m+1)!!} = G_k(\sigma^2, \gamma L^2) \\ & < \frac{e^{\sigma^2 k^2/2} - 1}{k(k-1)}. \end{aligned} \quad (8.38)$$

Then, we find $\sum_{i=1}^m (-\sigma^2)^i E_{k+m,k,i} = -\sigma^2 + F_{m,k}(\sigma^2)$ for $m \geq 2$ with $F_{m,k}(\sigma^2) = \sum_{i=2}^m (-\sigma^2)^i E_{k+m,k,i}$. In the large L limit we then have, for $\gamma > 0$,

$$G_k(\sigma^2, \gamma L^2) \rightarrow \sigma^2/2 + \lim_{L \rightarrow \infty} H_k(\sigma^2, \gamma L^2), \quad (8.39)$$

$$\begin{aligned} H_k(\sigma^2, \gamma L^2) &= \sum_{m=2}^{\infty} (-\gamma L^2)^m \frac{2^{m-1} F_{m,k}(\sigma^2)}{(m+1)(2m+1)!!} \\ &= (\gamma L^2)^2 M_k(\sigma^2, \gamma L^2), \end{aligned} \quad (8.40)$$

$$M_k(\sigma^2, \gamma L^2) = \sum_{m=0}^{\infty} (-\gamma L^2)^m \frac{2^{m+1} F_{m+2,k}(\sigma^2)}{(m+3)(2m+5)!!}.$$

In view of the H-stability upper bound of Eq. (8.38), M_k should be decaying as $1/L^4$ or faster, at large L . If it decays faster, then G_k is independent of k and the only possible state is a zero pressure one. If it decays as $1/L^4$, from the results of the appendix we can say that it does not increase with k and again the zero pressure state is the only one possible in the thermodynamic limit. So, in the end, we were unable to find a regular thermodynamics even for the repulsive stable case with positive γ . Everything is pointing towards a zero pressure state in the thermodynamic limit. This would be in agreement with the observation that as $\theta \rightarrow 0$ the only configurations contributing to the integral in Eq. (2.1) are the ones with minimum $V_N - \mu N$ which are those where the particles are infinitely spaced one another with $n \rightarrow 0$.

B. Observation

Now, we can observe that applying the previous analysis to the pairwise-additive Kac-Baker model, $v(x) = v_0 e^{-\gamma|x|}$, $\gamma > 0$, the structure of the solution for the partition function reads

$$\begin{aligned} \Omega &= 1 + \sum_{k=1}^{\infty} \frac{e^{-k^2 \sigma^2/2} (zL)^k}{k!} \sum_{n=k}^{\infty} f_{n,k}(\sigma^2) (\gamma L)^{n-k} \\ &= \Omega(zL, \sigma^2, \gamma L), \end{aligned} \quad (8.41)$$

with some given polynomials $f_{n,k}$. Again we can definitely say that the attractive model is thermodynamically unstable. But we know that the repulsive case is a pairwise-additive interaction model with a regular thermodynamics.

IX. CONCLUSIONS

We reviewed, under the unified setting of functional integration in one dimension, some of the exactly solvable one dimensional continuum fluid models of equilibrium classical statistical mechanics. Following the original idea of Marc Kac we write the partition function of each model as a path integral over particular Markoffian, Gaussian stochastic processes. Following the idea of Sam Edwards we further reduce the thermodynamic problem

for such fluids to the solution of a second order ordinary differential equation, the characteristic value problem.

In the work of Edwards and Lenard² it is also given a detailed analysis of how one can extend this method to get solutions for the pair- and higher orders static correlation functions.

We propose a generalization of the method which allows to treat other models with a non pairwise-additive interaction between the constituent penetrable particles of the fluid. The characteristic value problem of Edwards cannot be used anymore but the simplification of Kac remains valid. We apply this further developments to the simple case of the Gaussian core fluid model for which we prove that the attractive system is thermodynamically unstable, in agreement with the fact that it is not H-stable in the sense of Ruelle¹⁰, and find an approximate expression for the exact partition function in terms of a triple series one of which is alternating. We were unable to find a well defined thermodynamics even for the repulsive system. Everything suggest that the only admitted state in the thermodynamic limit is the zero pressure one.

Appendix A: The coefficients $E_{n,k,i}$

In table I we list the first exact $E_{n,k,i}$ coefficients for $i = 2, 3, 4$ and the first seven n .

From the table we can see how there is a very weak dependence on k . So we can on a first ground assume that $E_{n,k,i} \approx E_{n,2,i} = e_{n-i,i}$ for all k . Moreover the entries of the table satisfy the following recurrence relation

$$e_{2,i} = 1, \quad (A1)$$

$$e_{j,2} = 2^{j-1} - 1, \quad (A2)$$

$$e_{j,i} = i e_{j-1,i} + e_{j,i-1}, \quad (A3)$$

with $j = n - i$. So that introducing the generating function $\varphi(x, i) = \sum_{j=2}^{\infty} e_{j,i} x^j$ we easily find

$$\varphi(x, 2) = x^2 / (x-1)(2x-1), \quad (A4)$$

$$\varphi(x, i)/x = i \varphi(x, i) + \varphi(x, i-1)/x, \quad (A5)$$

with solution

$$\varphi(x, i) = \frac{x^3}{(x-1)(-x)^i (2-1/x)_{i-1}}, \quad (A6)$$

with $(a)_i = a(a+1) \cdots (a+i-1) = \Gamma(a+i)/\Gamma(a)$ the Pochhammer symbol. The desired coefficient $e_{j,i}$ is the j -th coefficient in the series expansion of $\varphi(x, i)$ around $x = 0$.

More precisely we can then write $E_{n,k,i} = h_{n,k,i} e_{n-i,i}$ with $h_{n,2,i} = 1$ and $E_{2+i,2,i} = 1$. We can also observe that $E_{n,k,i}$ tends to decrease with k at fixed n and i .

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TABLE I. Exact $E_{n,k,i}$ for $i = 2, 3, 4$.

$E_{n,k,2}$	$n = 7$	$n = 6$	$n = 5$	$n = 4$
$k = 2$	15	7	3	1
$k = 3$	5105/352	79/12	33/14	
$k = 4$	211/18	243/56		
$k = 5$	389/56			

$E_{n,k,3}$	$n = 7$	$n = 6$	$n = 5$
$k = 2$	25	6	1
$k = 3$	4923/176	31/6	
$k = 4$	17		

$E_{n,k,4}$	$n = 7$	$n = 6$
$k = 2$	10	1
$k = 3$	965/88	

$E_{n,k,2}$	$n = 7$	$n = 6$	$n = 5$	$n = 4$
$k = 2$	15	7	3	1
$k = 3$	14.5	6.6	2.4	
$k = 4$	11.7	4.3		
$k = 5$	6.9			

$E_{n,k,3}$	$n = 7$	$n = 6$	$n = 5$
$k = 2$	25	6	1
$k = 3$	28.0	5.2	
$k = 4$	17		

$E_{n,k,4}$	$n = 7$	$n = 6$
$k = 2$	10	1
$k = 3$	11.0	

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